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04AUG95 E136036-1 C03022
P01/7700 25.00

-2 AUG 1995

Your reference
8651

Notes
Please type, or write in dark ink using CAPITAL letters. A prescribed fee is payable for a request for grant of a patent. For details, please contact the Patent Office (telephone 071-438 4700).

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The Patent Office

Request for grant of a Patent

Form 1/77

Patents Act 1977

❶ Title of invention

1 Please give the title of the invention — ESTER SYNTHESIS

❷ Applicant's details

❑ **First or only applicant**

2a If you are applying as a corporate body please give:

Corporate name — BP CHEMICALS LIMITED

Country *(and State of incorporation, if appropriate)* — ENGLAND, UNITED KINGDOM

2b If you are applying as an individual or one of a partnership please give in full:

Surname

Forenames

2c **In all cases**, please give the following details:

Address — BRITANNIC HOUSE
1 FINSBURY CIRCUS
LONDON

UK postcode *(if applicable)* — EC2M 7BA

Country — ENGLAND, UNITED KINGDOM

ADP number *(if known)* — 4141891002

2d, 2e and 2f: If there are further applicants please provide details on a separate sheet of paper.

☐ **Second applicant *(if any)***

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❸ Address for service details

3a Have you appointed an agent to deal with your application?

Yes [X] No [ ] ➡ ***go to 3b***

⬇ ***please give details below***

Agent's name KRISHNAN, Suryanarayana Kalyana

Agent's address BP INTERNATIONAL LIMITED
Group Patents & Agreements
Chertsey Road
Sunbury-on-Thames
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Postcode TW16 7LN

Agent's ADP number 568392S001

3b: If you have appointed an agent, all correspondence concerning your application will be sent to the agent's United Kingdom address.

3b If you have not appointed an agent please give a name and address in the United Kingdom to which all correspondence will be sent:

Name

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ADP number *(if known)*

❹ Reference number

4 Agent's or applicant's reference number *(if applicable)* 8651

❺ Claiming an earlier application date

5 Are you claiming that this application be treated as having been filed on the date of filing of an earlier application?

Please mark correct box

Yes ☐ No ☒ ➡ ***go to 6***

↓ ***please give details below***

❑ number of earlier application or patent number

❑ filing date *(day month year)*

❑ and the Section of the Patents Act 1977 under which you are claiming:

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15(4) (Divisional) ☐ 8(3) ☐ 12(6) ☐ 37(4) ☐

❻ Declaration of priority

❻ If you are declaring priority from a PCT Application please enter 'PCT' as the country and enter the country code (for example, GB) as part of the application number.

Please give the date in all number format, for example, 31/05/90 for 31 May 1990.

6 If you are declaring priority from previous application(s), please give:

Country of filing	Priority application number *(if known)*	Filing date *(day, month, year)*

❼ *The answer must be 'No' if:*
- *any applicant is not an inventor*
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- *any applicant is a corporate body.*

❼ Inventorship

7 Are you (the applicant or applicants) the sole inventor or the joint inventors?

Please mark correct box

Yes [ ] No [X] ➡ ***A Statement of Inventorship on Patents Form 7/77 will need to be filed (see Rule 15).***

❽ *Please supply duplicates of claim(s), abstract, description and drawing(s).*

❽ Checklist

8a Please fill in the number of sheets for each of the following types of document contained in this application.

		Continuation sheets for this Patents Form 1/77	–
Claim(s)	–	Description	4
Abstract	–	Drawing(s)	–

8b Which of the following documents also accompanies the application?

Please mark correct box(es)

Priority documents *(please state how many)*	
Translation(s) of Priority documents *(please state how many)*	
Patents Form 7/77 – Statement of Inventorship and Right to Grant *(please state how many)*	
Patents Form 9/77 – Preliminary Examination/Search	
Patents Form 10/77 – Request for Substantive Examination	

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❾ Request

I/We request the grant of a patent on the basis of this application.

Please sign here ➡ Signed [signature] Date 02 08 1995 *(day month year)*

KRISHNAN, Suryanarayana Kalyana

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ESTER SYNTHESIS

The present invention relates to a process for the synthesis of esters by reacting an olefin with a lower carboxylic acid in the presence of an acidic catalyst.

It is well known olefins can be reacted with lower aliphatic carboxylic acids to form the corresponding esters. One such method is described in GB-A-1259390 in which an ethylenically unsaturated compound is contacted with a liquid medium comprising a carboxylic acid, a free heteropoly acid of molybdenum or tungsten. This process is a homogeneous process in which the heteropolyacid catalyst is unsupported. A further process for producing esters is described in JP-A-05294894 in which a lower fatty acid is esterified with a lower olefin to form a lower fatty acid ester. In this document, the esterification reaction is carried out in the gaseous phase in the presence of a catalyst consisting of at least one heteropolyacid salt of a metal eg Li, Cu, Mg or K, being supported on a carrier. The heteropolyacid used is phosphotungstic acid and the carrier described is silica.

It has now been found that the process efficiency can be improved significantly by using a specific carrier.

Accordingly, the present invention is a process for the production of lower aliphatic esters said process comprising reacting a lower olefin with a saturated lower aliphatic mono-carboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst on a siliceous support characterised in that the siliceous support is in the form of extrudates or pellets.

The siliceous support used is most preferably derived from an amorphous, non-porous synthetic silica especially fumed silica, such as those produced by flame hydrolysis of $SiCl_4$. Specific examples of such siliceous supports include Support 350

made by pelletisation of AEROSIL® 200 (both ex Degussa). This pelletisation procedure is suitably carried out by the process described in US Patent 5,086,031 (see especially the Examples) and is incorporated herein by reference. Such a process of pelletisation or extrusion does not involve any steam treatment steps and the porosity of the support is derived from the interstices formed during the pelletisation or extrusion step of the non-porous silica. The silica support is suitably in the form of pellets or beads or are globular in shape having a particle diameter of 2 to 10 mm, preferably 4 to 6 mm. The siliceous support suitably has a pore volume in the range from 0.3-1.2 ml/g, preferably from 0.6-1.0 ml/g. The support suitably has a crush strength of at least 2 Kg force, suitably at least 5 Kg force, preferably at least 6 Kg and more preferably at least 7 Kg. The crush strengths quoted are based on average of that determined for each set of 50 beads/globules on a CHATTILLON tester which measures the minimum force necessary to crush a particle between parallel plates. The bulk density of the support is suitably at least 380 g/l, preferably at least 440 g/l.

The support suitably has an average pore radius (prior to use) of 10 to 500 Angstroms, preferably an average pore radius of 30 to 100 Angstroms.

In order to achieve optimum performance, the siliceous support is suitably free of extraneous metals or elements which might adversely affect the catalytic activity of the system. The siliceous support suitably has at least 99% w/w purity, ie the impurities are less than 1% w/w, preferably less than 0.60% w/w and more preferably less than 0.30% w/w.

The term "heteropolyacids" as used herein and throughout the specification is meant to include the free acids. The heteropolyacids used to prepare the olefin hydration catalysts of the present invention therefore include the free acids in which the anion is a complex, high molecular weight entity. Typically, the anion is comprises 2-18 oxygen-linked polyvalent metal atoms, which are called peripheral atoms. These peripheral atoms surround one or more central atoms in a symmetrical manner. The peripheral atoms are usually one or more of molybdenum, tungsten, vanadium, niobium, tantalum and other metals. The central atoms are usually silicon or phosphorus but can comprise any one of a large variety of atoms from Groups I-VIII in the Periodic Table of elements. These include, for instance, cupric ions; divalent beryllium, zinc, cobalt or nickel ions; trivalent boron, aluminium, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium or rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, tellurium, manganese nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent

phosphorus, arsenic, vanadium, antimony ions; hexavalent tellurium ions; and heptavalent iodine ions. Such heteropolyacids are also known as "polyoxoanions", "polyoxometallates" or "metal oxide clusters". The structures of some of the well known anions are named after the original researchers in this field and are known eg as Keggin, Wells-Dawson and Anderson-Evans-Perloff structures.

Heteropolyacids usually have a high molecular weight eg in the range from 700-8500 and include dimeric complexes. They have a relatively high solubility in polar solvents such as water or other oxygenated solvents, especially if they are free acids and in the case of several salts, and their solubility can be controlled by choosing the appropriate counterions. Specific examples of heteropolyacids that may be used as the catalysts in the present invention include:

12-tungstophosphoric acid	- $H_3[PW_{12}O_{40}].xH_2O$
12-molybdophosphoric acid	- $H_3[PMo_{12}O_{40}].xH_2O$
12-tungstosilicic acid	- $H_4[SiW_{12}O_{40}].xH_2O$
12-molybdosilicic acid	- $H_4[SiMo_{12}O_{40}].xH_2O$
Potassium tungstophosphate	- $K_6[P_2W_{18}O_{62}].xH_2O$
Sodium molybdophosphate	- $Na_3[PMo_{12}O_{40}].xH_2O$
Ammonium molybdodiphosphate	- $(NH_4)_6[P_2Mo_{18}O_{62}].xH_2O$
Sodium tungstonickelate	- $Na_4[NiW_6O_{24}H_6].xH_2O$
Ammonium molybdodicobaltate	- $(NH_4)[Co_2Mo_{10}O_{36}].xH_2O$
Cesium hydrogen tungstosilicate	- $Cs_3H[SiW_{12}O_{40}].xH_2O$
Potassium molybdodivanado phosphate	- $K_5[PMoV_2O_{40}].xH_2O$

The impregnated support is suitably prepared by dissolving the heteropolyacid, which is preferably a tungstosilicic acid, in eg distilled water, and then adding the support to the aqueous solution so formed. The support is suitably left to soak in the acid solution for a duration of several hours, with periodic manual stirring, after which time it is suitably filtered using a Buchner funnel in order to remove any excess acid.

The wet catalyst thus formed is then suitably placed in an oven at elevated temperature for several hours to dry, after which time it is allowed to cool to ambient temperature in a dessicator. The weight of the catalyst on drying, the weight of the support used and the weight of the acid on support was obtained by deducting the latter from the former from which the catalyst loading in g/litre was determined.

This catalyst (measured by weight) can then be used in the esterification process. The amount of heteropolyacid deposited/impregnated on the support for use in the esterification reaction is suitably in the range from 10 to 60% by

weight, preferably from 30 to 50% by weight.

In the esterification reaction, the olefin reactant used is suitably ethylene, propylene or mixtures thereof. Where a mixture of olefins is used, the resultant product will inevitably a mixture of esters. The source of the olefin reactant used may be a refinery product or a chemical grade olefin which invariably contain some alkanes admixed therewith.

The saturated, lower aliphatic mono-carboxylic acid reactant is suitably a C1-C4 carboxylic acid and is preferably acetic acid.

The reaction mixture suitably comprises a molar excess of the acid with respect to the olefin reactant.

The reaction is carried out in the vapour phase suitably above the dew point of the reactor contents comprising the reactant acid, any alcohol formed *in situ*, the product ester and optionally some water. Dew point is the temperature at which condensation of a vapour of a given sample in air takes place. The dew point of any vaporous sample will depend upon its composition. The supported heteropolyacid catalyst is suitably used as a fixed bed which may be in the form of a packed column. The vapours of the reactant olefins and acids are passed over the catalyst suitably at an GHSV of 100 to 5000 per hour, preferably from 300 to 2000 per hour.

The esterification reaction is suitably carried out at a temperature in the range from 150-200°C using a reaction pressure which is at least 400KPa, preferably from 500-700 KPa.

The reaction mixture may optionally contain steam if it is desired to generate a mixture of esters and alcohols in the process. The products of the reaction are recovered by eg fractional distillation. Where the esters are produced, whether singly or as mixture of esters, these may be hydrolysed to the corresponding alcohols or mixture of alcohols in relatively high yields and purity. By using this latter technique the efficiency of the process to produce alcohols from olefins is significantly improved over the conventional process of producing alcohols by hydration of olefins.